

APPENDIX: THE DIELECTRIC SUSCEPTIBILITY

A General *Dressed State* Formulation

Suppose that the complete Hamiltonian of a coupled system is parsed into two components

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{ex} . \quad [\text{VA-1}]$$

The component \mathcal{H}_o includes the Hamiltonians for the unperturbed material system, the free radiation field and interactions of the material system with available *cavity modes*. The component \mathcal{H}_{ex} is the Hamiltonian for the interactions which couple the material system to **externally excited modes**. As the first step in finding a fully quantal expression for the dielectric susceptibility, let us expand the state vector in the Schrödinger picture in terms of, presumably, known eigenkets of \mathcal{H}_o -- viz. the *dressed states* of the unperturbed system --

$$| (t) \rangle = \sum_s C_s(t) \exp(-i \epsilon_s t) |s\rangle . \quad [\text{VA-2}]$$

Following a now familiar track, we can use the Schrödinger equation of motion -- *i.e.*

$$i \hbar \frac{d}{dt} | (t) \rangle = [\mathcal{H}_o + \mathcal{H}_{ex}] | (t) \rangle \quad [\text{VA-3}]$$

to obtain

$$\begin{aligned} i \hbar \dot{C}_r(t) &= \sum_q C_q(t) \exp[-i (\epsilon_q - \epsilon_r) t] \langle r | \mathcal{H}_{ex} | q \rangle \\ -i \hbar \dot{C}_q(t) &= \sum_r C_r(t) \exp[+i (\epsilon_q - \epsilon_r) t] \langle q | \mathcal{H}_{ex} | r \rangle . \end{aligned} \quad [\text{VA-4}]$$

In turn, we obtain the following expansion for the time dependent expectation value of induced material system dipole moment:

$$\begin{aligned}
\langle \vec{\mathbf{p}}(t) \rangle &= -\langle (t) | e \vec{\mathcal{D}} | (t) \rangle \\
&= - \sum_r C_r(t) \exp[i \omega_r t] \langle r | e \vec{\mathcal{D}} \sum_s C_s(t) \exp[-i \omega_s t] | s \rangle \quad [\text{VA-5}] \\
&= - \sum_r \sum_s C_r(t) C_s(t) \exp[i (\omega_r - \omega_s) t] e \langle r | \vec{\mathcal{D}} | s \rangle
\end{aligned}$$

Differentiating this expression with respect to time and using Equation [VA-4] we obtain

$$\begin{aligned}
\langle \dot{\vec{\mathbf{p}}}(t) \rangle &= - \sum_r \sum_s i \sum_q C_q(t) C_s(t) \exp[i (\omega_q - \omega_s) t] \langle q | \mathcal{H}_{ex} | r \rangle \frac{e}{\hbar} \langle r | \vec{\mathcal{D}} | s \rangle \\
&\quad + \sum_r \sum_s i \sum_q C_r(t) C_q(t) \exp[-i (\omega_q - \omega_r) t] \langle s | \mathcal{H}_{ex} | q \rangle \frac{e}{\hbar} \langle r | \vec{\mathcal{D}} | s \rangle \quad [\text{VA-6a}] \\
&\quad - \sum_r \sum_s C_r(t) C_s(t) i (\omega_r - \omega_s) \exp[i (\omega_r - \omega_s) t] e \langle r | \vec{\mathcal{D}} | s \rangle
\end{aligned}$$

Regrouping, we see that this expression can be written

$$\begin{aligned}
\langle \dot{\vec{\mathbf{p}}}(t) \rangle &= - \sum_r \sum_s \frac{i e}{\hbar} \sum_q C_q(t) C_s(t) \exp[i (\omega_q - \omega_s) t] \left[\langle q | \mathcal{H}_{ex} | r \rangle \langle r | \vec{\mathcal{D}} | s \rangle - \langle r | \mathcal{H}_{ex} | s \rangle \langle q | \vec{\mathcal{D}} | r \rangle \right] \\
&\quad - \sum_r \sum_s C_r(t) C_s(t) i (\omega_r - \omega_s) \exp[i (\omega_r - \omega_s) t] e \langle r | \vec{\mathcal{D}} | s \rangle \quad [\text{VA-6b}]
\end{aligned}$$

Since \mathcal{H}_{ex} is proportional to $\vec{\mathcal{D}}$, we see that, *like magic*, the first term vanishes!!!

Hence,

$$\langle \dot{\vec{\mathbf{p}}}(t) \rangle = - \sum_r \sum_s C_r(t) C_s(t) i (\omega_r - \omega_s) \exp[i (\omega_r - \omega_s) t] e \langle r | \vec{\mathcal{D}} | s \rangle. \quad [\text{VA-6c}]$$

Differentiating this expression with respect to time and, again, using Equation [VA-4] we obtain

$$\begin{aligned}
\langle \ddot{\vec{p}}(t) \rangle = & - \sum_{r,s,q} C_q(t) C_s(t) \frac{e}{\hbar} \exp[i(\omega_q - \omega_s)t] \\
& \times \left[(\omega_r - \omega_s) \langle q | \mathcal{H}_{ex} | r \rangle \langle r | \vec{\mathcal{D}} | s \rangle + (\omega_r - \omega_q) \langle q | \vec{\mathcal{D}} | r \rangle \langle r | \mathcal{H}_{ex} | s \rangle \right] \quad [\text{VA-7}] \\
& - \sum_{r,s} C_r(t) C_s(t) (\omega_r - \omega_s)^2 \exp[i(\omega_r - \omega_s)t] e \langle r | \vec{\mathcal{D}} | s \rangle
\end{aligned}$$

Our task is to now to attempt an interpretation this very nasty expression. To that end, we make use of Equation [V-33] to write Equation [VA-6c] as

$$\begin{aligned}
\langle \vec{p}(t) \rangle = & - \sum_{r,s} C_r(t) C_s(t) \exp[i(\omega_r - \omega_s)t] \\
& \times e \langle r | \left\{ \langle a | \vec{\mathcal{D}} | b \rangle U_{t1} \mu_t^\dagger + \langle b | \vec{\mathcal{D}} | a \rangle U_{t1} \mu_t \right\} | s \rangle \quad [\text{VA-8a}]
\end{aligned}$$

Using the properties of the μ_t^\dagger and μ_t operators (*viz.* $|s\rangle = \mu_s^\dagger |g\rangle$ and $|g\rangle = \mu_s |s\rangle$), this expression reduces to

$$\langle \vec{p}(t) \rangle = - \sum_{r,s} C_r(t) C_s(t) \exp[i(\omega_r - \omega_s)t] e \left\{ \langle a | \vec{\mathcal{D}} | b \rangle U_{r1} \mu_{sg} + \langle b | \vec{\mathcal{D}} | a \rangle U_{s1} \mu_{rg} \right\} \quad [\text{VA-8b}]$$

which may interpreted as a sum of a series of dipole moment components -- *viz.*

$$\langle \vec{p}(t) \rangle = \sum_s \vec{p}_s(t) = - \sum_s \left\{ C_s(t) C_g(t) \exp[i(\omega_s - \omega_g)t] e \langle a | \vec{\mathcal{D}} | b \rangle U_{s1} + c.c. \right\} \quad [\text{VA-8c}]$$

Given this interpretation, we return to Equation [VA-7] and use Equation [V-6] to obtain

$$\begin{aligned}
\langle \ddot{\vec{p}}(t) \rangle = & + \sum_{r,s,q} C_q(t) C_s(t) \frac{e^2}{\hbar} [2(\omega_r - \omega_s - \omega_q) \times \exp[i(\omega_q - \omega_s)t] \vec{E}_T(0) \langle q | \vec{\mathcal{D}} | r \rangle \langle r | \vec{\mathcal{D}} | s \rangle \\
& + \sum_{r,s} C_r(t) C_s(t) (\omega_r - \omega_s)^2 \exp[i(\omega_r - \omega_s)t] e \langle r | \vec{\mathcal{D}} | s \rangle \quad .[\text{VA-9}]
\end{aligned}$$

Again using Equation [V-33] and the properties of the μ_r^\dagger and μ_r operators, we see that

$$\begin{aligned}
 \langle q | \vec{\mathcal{D}} | r \rangle \langle r | \vec{\mathcal{D}} | s \rangle &= \langle q | \left\{ \langle a | \vec{\mathcal{D}} | b \rangle U_{x1} \mu_x^\dagger + \langle b | \vec{\mathcal{D}} | a \rangle U_{x1} \mu_x \right\} | r \rangle \\
 &\quad \times \langle r | \left\{ \langle a | \vec{\mathcal{D}} | b \rangle U_{y1} \mu_y^\dagger + \langle b | \vec{\mathcal{D}} | a \rangle U_{y1} \mu_y \right\} | s \rangle \\
 &= \sum_x \sum_y \left\{ \langle a | \vec{\mathcal{D}} | b \rangle^2 U_{x1} U_{y1} \langle q | \mu_x^\dagger | r \rangle \langle r | \mu_y^\dagger | s \rangle \right. \\
 &\quad + \left| \langle a | \vec{\mathcal{D}} | b \rangle \right|^2 U_{x1} U_{y1} \langle q | \mu_x^\dagger | r \rangle \langle r | \mu_y | s \rangle \\
 &\quad + \langle b | \vec{\mathcal{D}} | a \rangle^2 U_{x1} U_{y1} \langle q | \mu_x | r \rangle \langle r | \mu_y | s \rangle \\
 &\quad \left. + \left| \langle b | \vec{\mathcal{D}} | a \rangle \right|^2 U_{x1} U_{y1} \langle q | \mu_x | r \rangle \langle r | \mu_y^\dagger | s \rangle \right\} \quad [\text{VA-10a}]
 \end{aligned}$$

which reduces to

$$\langle q | \vec{\mathcal{D}} | r \rangle \langle r | \vec{\mathcal{D}} | s \rangle = \langle a | \vec{\mathcal{D}} | b \rangle \langle b | \vec{\mathcal{D}} | a \rangle U_{q1} U_{s1} + \langle b | \vec{\mathcal{D}} | a \rangle \langle a | \vec{\mathcal{D}} | b \rangle |U_{r1}|^2 \quad [\text{VA-10b}]$$

Substituting this expression and the expression in Equation [V-33] into Equation [VA-9] and, again, using the properties of the μ_r^\dagger and μ_r operators it is relatively straightforward to obtain

$$\begin{aligned}
 \left\langle \ddot{\mathbf{p}}(t) \right\rangle + \sum_s \bar{\mathbf{p}}_s(t) &= -\frac{e^2}{\hbar} \sum_q \left[\sum_s + \sum_q \right] C_q(t) C_s(t) U_{q1} U_{s1} \\
 &\quad \times \exp \left[i \left(\omega_q - \omega_s \right) t \right] \bar{\mathbf{E}}_T(0) \langle a | \vec{\mathcal{D}} | b \rangle \langle b | \vec{\mathcal{D}} | a \rangle. \quad [\text{VA-11a}] \\
 &\quad + \frac{e^2}{\hbar} \sum_r 2 \left| C_r(t) \right|^2 |U_{r1}|^2 \bar{\mathbf{E}}_T(0) \langle b | \vec{\mathcal{D}} | a \rangle \langle a | \vec{\mathcal{D}} | b \rangle
 \end{aligned}$$

Thus, in a kind of *rotating field approximation*, we get a set of driven harmonic oscillator equations of the form

$$\ddot{\vec{p}}_s(t) + \frac{2}{s} \vec{p}_s(t) = \frac{e^2}{\hbar} \vec{E}_T(0) \left| \langle a | \vec{\mathcal{D}} | b \rangle \right|^2 \frac{2}{s} \left| C_g(t) \right|^2 - \left| C_s(t) \right|^2 \left| U_{sl} \right|^2. \quad [\text{VA-11b}]$$

In the Weisskopf-Wigner approximation¹ -- i.e. $\left| C_g(t) \right|^2 \approx 1$ -- we can easily solve these equations and sum their results to obtain a *standardized form* for the frequency dependent of the **dressed** dielectric susceptibility of the system

$$\begin{aligned} \chi(\omega) &= \frac{N e^2}{\hbar} \left| \langle a | \vec{\mathcal{D}} | b \rangle \right|^2 \frac{2}{s} \frac{1}{s^2 - \omega^2} \left| U_{rl} \right|^2 \\ &= \frac{N e^2}{\hbar} \left| \langle a | \vec{\mathcal{D}} | b \rangle \right|^2 \left| U_{rl} \right|^2 \left[\frac{1}{s - \omega} + \frac{1}{s + \omega} \right] \end{aligned} \quad [\text{VA-12}]$$

¹ V. Weisskopf and E. Wigner, Z. Phys., **63**, 54 (1930).